

# PATENT SPECIFICATION

NO DRAWINGS

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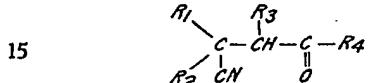
## COMPLETE SPECIFICATION

### $\beta,\beta$ -Disubstituted- $\beta$ -cyanoketones

We, ROHM & HAAS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of 222, West Washington Square, Philadelphia 5, Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and 10 by the following statement:—

This invention is concerned with new  $\beta,\beta$ -disubstituted- $\beta$ -cyanoketones.

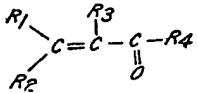
In brief, this invention provides new  $\beta,\beta$ -disubstituted- $\beta$ -cyanoketones of the formula:



in which  $R_1$ ,  $R_4$  and  $R_4$  are alkyl or cycloalkyl groups and  $R_3$  is a hydrogen atom or a methyl, ethyl or pentyl group, the number of carbon atoms, including the cyano carbon atoms, in the compounds ranging from 13 to 25.

It is preferred that  $R_3$  is hydrogen, methyl or ethyl and that either one or two of the symbols  $R_1$ ,  $R_2$  and  $R_4$  represent methyl groups. The groups of  $R_1$ ,  $R_2$  and  $R_4$ , which are preferably alkyl, may be present in any of the known isomeric forms.

The compounds of this invention are prepared by the hydrocyanation of a  $C_{13-24}$  unsaturated ketone of the formula:



where  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are as above defined. This hydrocyanation is carried out by bringing together hydrocyanic acid and the unsaturated ketone at a temperature in the range from about 125° to 275° C. and in the presence of an alkaline catalyst capable of generating cyanide ions, the hydrocyanic acid being

gradually brought into contact with the unsaturated ketone at a rate which is substantially that at which it reacts with the ketone.

Typical of the  $\beta,\beta$ -disubstituted- $\alpha,\beta$ -olefinic ketone reactants that may be employed are 40 4 - methylundec - 3 - en - 2 - one, 3,4-dimethylundec - 3 - en - 2 - one, 4 - methyl-3 - ethyldodec - 3 - en - 2 - one, 4 - methyltridec - 3 - en - 2 - one, 3,4 - dimethylhexadec - 3 - en - 2 - one, 3 - ethyl - 4 - methyloctadec - 3 - en - 2 - one, 2 - methylundec - 2 - en - 4 - one, 2,3 - dimethylundec - 2 - en - 4 - one, 2 - methyl - 3 - ethyldodec - 2 - en - 4 - one, 2 - methyltetradec - 2 - en - 4 - one, 2,3 - dimethylhexadec - 2 - en - 4 - one, 2 - methyl-3 - ethyloctadec - 2 - en - 4 - one, 4 - 50 butyloctadec - 3 - en - 2 - one, 3 - methyl-4 - hexylnonadec - 3 - en - 2 - one, 3 - ethyl - 4 - pentylundec - 3 - en - 2 - one, 4 - octylhexadec - 3 - en - 2 - one, 5 - methylundec - 5 - en - 7 - one, 5,6 - diethyldodec - 5 - en - 4 - one, 8,9 - dimethyloctadec - 8 - en - 7 - one, 4 - methyl-5 - ethylnonadec - 4 - en - 6 - one, 7 - methylpentadec - 7 - en - 9 - one, 2,6,8-trimethylnon - 5 - en - 4 - one, 7 - pentyltridec - 6 - en - 5 - one, 5 - ethyl - 6 - hexylhexadec - 5 - en - 4 - one, 3,4 - diethyloctadec - 3 - en - 5 - one, 2,2,5,7,7-pentamethylhept - 4 - en - 3 - one, 8 - methyltridec - 7 - en - 6 - one, 1,3 - di-cyclohexylbut - 2 - en - 1 - one, 11 - methylnonadec - 10 - en - 9 - one, 3 - pentyl - 4 - methylundec - 3 - en - one, 2,2,4,8,10,12,12 - heptamethyl - tridec - 7 - en - 6 - one, and 2,4,6,9,10,12,14 - heptamethylpentadec - 8 - en - 7 - one.

The  $\alpha,\beta$ -unsaturated ketone reactant employed in the process of the invention is frequently present in the form of a mixture with the corresponding  $\beta,\gamma$ -unsaturated tautomers. The  $\beta,\gamma$ -unsaturated compounds will themselves, in the presence of basic compounds, form mixtures of  $\alpha,\beta$ - and  $\beta,\gamma$ -

unsaturated tautomers and can therefore be used as a source of the  $\alpha,\beta$ -unsaturated tautomer. Such a mixture can be employed in the process of the invention and the term 5  $\alpha,\beta$ -unsaturated ketone reactant used herein is to be construed as embracing such tautomeric mixtures. Typical  $\beta,\gamma$ -unsaturated tautomers are as follows:—

10 5-methylundec-4-en-7-one,  
2,4,8-trimethyl-non-3-en-6-one,  
7-methylpentadec-6-en-9-one,  
3-pentyl-4-methyldec-4-en-2-one,  
3-penyl-4-hexyl-pent-4-en-2-one, and  
3-(1-methylheptyl)-oct-4-en-2-one.

15 As indicated, the hydrocyanation reaction is conducted at a temperature in the range of about 125° to 275° C., this is so because temperatures outside of this range either result in inappreciable or undesirable results.

20 The preferred temperature range is from 150° to 225° C.

25 Atmospheric pressure is advantageously employed. Superatmospheric pressures may be employed, if desired, but apparently no appreciable advantages are achieved thereby. If superatmospheric pressures are contemplated, they may be achieved autogenously or with the aid of nitrogen or other inert gas.

30 The present reaction is preferably conducted on a batch basis but a continuous adaptation may be employed, if desired.

35 A volatile inert highly polar organic solvent may be employed, if desired. The use of a solvent is especially desirable when the higher-boiling ketone reactants are used. It is frequently desirable to employ a portion of the specific  $\beta,\beta$ -distubstituted- $\beta$ -cyano-ketone product concerned in the present method as a solvent. Suitable solvents include dimethylformamide, dimethylacetamide, 1-methyl-2-pyrrolidinone, 1,5-dimethyl-2-pyrrolidinone and 1,3-dimethyl-2-imidazolidinone.

40 45 An alkaline catalyst capable of generating cyanide ions is required, and is preferably used in amounts of about 0.1 to 20% by weight of the total weight of the reactants. Suitable in this respect are alkali metals and their carbonates; alkali and alkaline earth metal alkoxides, oxides, hydroxides, peroxides, and cyanides; *tert*-amines; and quaternary ammonium bases. Actually, there may be employed as catalyst any base which has an ionization constant above about  $10^{-7}$  when determined in an aqueous medium. Typical examples of the catalysts that may be used include sodium, potassium, lithium, sodium methoxide, potassium butoxide, lithium ethoxide, magnesium ethoxide, sodium oxide, potassium hydroxide, calcium oxide, barium hydroxide, strontium hydroxide, sodium peroxide, magnesium peroxide, potassium cyanide, lithium cyanide, barium cyanide, magnesium cyanide, sodium carbonate, potas-

sium carbonate, trimethylamine, triethylamine, triethanolamine, octyldimethylamine, N-methylmorpholine, benzyltrimethylammonium hydroxide, dibenzyltrimethylammonium hydroxide, and dodecetyltrimethylammonium hydroxide. The alkali metal cyanides are particularly effective for the instant purposes.

50 A preferred feature of the process involves bringing together, at the specified reaction temperature, preformed mixtures of (a) the alkaline catalyst and the  $\alpha,\beta$ -unsaturated ketone reactant or the desired cyanoketone product and (b) hydrocyanic acid and the unsaturated  $\alpha,\beta$ -unsaturated ketone reactant.

55 By employing the most preferred reaction conditions described above, yields of about 55 to 90% and above can be consistently achieved. Under these preferred reaction conditions, there is substantially no polymerization of the hydrocyanic acid and there are substantially no cyclization, condensation, or decomposition compounds formed, either or both of which undesired results frequently harass the cyanation procedures known to the art.

60 In a practical way of carrying out the process, whether the continuous or batch embodiment is used, the catalyst and a portion of the ketone reactant is initially charged to the reaction vessel and to this mixture there is then added a mixture of the same ketone reactant and hydrocyanic acid. Alternatively, it is possible to use as an initial charge to the reaction vessel a mixture of catalyst with a portion of the ketone nitrile product from a previous run, to this mixture being added a mixture of hydrocyanic acid and ketone reactant. By employing, as part of the initial charge, the ketone reactant or the ketone nitrile product, the formation of undesired condensation products is reduced to a minimum or entirely eliminated. This leads to maximum yields with minimum amounts of undesired products, which minimizes or substantially eliminates problems of separation and isolation of the product. It is also satisfactory in the present invention, when either a batch or continuous embodiment is used, to add all of the catalyst at the beginning of the reaction or intermittently, as desired. It should, however, be particularly noted that the hydrocyanic acid mixture should be gradually brought into contact with the catalyst mixture at a rate which is substantially that at which the hydrocyanic acid reacts with the  $\alpha,\beta$ -unsaturated ketone reactant. With large amounts of hydrocyanic acid present at any one time, undesired polymerizations tend to be favoured.

65 It is possible, in carrying out the reaction, to introduce the hydrocyanic acid into the reaction zone in the gaseous state. In some cases, it may be that the catalyst is not soluble or at least not entirely soluble in the reaction system, and it is therefore,

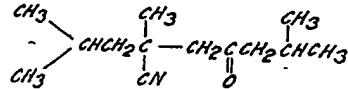
desirable to employ agitation such as stirring or rocking or the like in order to insure the highest activity from the catalyst. Agitation of the reaction system is generally advantageous.

At the conclusion of the reaction, the catalyst may be neutralized by the addition of acid, preferably of a mineral acid such as phosphoric, sulfuric or hydrochloric. The reaction mixture may then be filtered, if desired, and then distilled, preferably at reduced pressures. The products are colorless liquids and are useful as insecticides and as solvents for polymers. The products are particularly useful against the red spider and the rice weevil. They apparently are more effective against the red spider when employed as a spray in an inert hydrocarbon solvent base. The compounds are preferably used against the rice weevil in the form of a 10% dust in an inert commercial base.

25 The present invention may be more fully understood from the following examples, which are offered by way of illustration and not by way of limitation. Parts by weight are used throughout.

**EXAMPLE 1**

30 A mixture of 109 parts of 2,4,8-trimethyl-  
non-4-en-6-one [and its tautomers 2,4,8-tri-  
methylnon-3-en-6-one and 2(2-methylpropyl)-  
6-methylhept-1-en-4-one], dimethylformamide  
(109 parts) and potassium cyanide (2 parts)  
is heated under reflux (159° C.). A mixture  
35 of hydrocyanic acid (17 parts) and dimethyl-  
formamide (17 parts) is added dropwise  
during 2.25 hours at a rate such that the  
pot temperature is maintained in the region  
of 147° to 159° C. during the entire time.  
40 The mixture is heated under reflux for an  
additional period of 1.25 hours and then  
is cooled and treated with aqueous 85%  
phosphoric acid (2.3 parts). The mixture  
is distilled under reduced pressure. The  
45 product (92 parts—73% yield) is a colorless  
liquid that boils at 140° to 141° C. at  
10 mm. absolute pressure. It has an  $n_D^{25}$   
value of 1.4431 and contains 6.45% nitrogen  
(theoretical for  $C_{13}H_{26}ON$ —6.70%). The pro-  
50 duct is identified as 2,4,8-trimethyl-4-cyano-6-  
nonanone and corresponds to the formula



### EXAMPLE 2

55 A mixture of 7-methylpentadec-7-en-9-one (214.2 parts), dimethylacetamide (100 parts) and potassium carbonate (3 parts) is heated to 170° C. A mixture of hydrocyanic acid (25.5 parts) and dimethylacetamide (25 parts) is added at a rate such that the temperature

is maintained at the level of at least 160° C. The mixture is heated 1.0 hour after the addition is completed and then cooled and treated with aqueous 85% phosphoric acid (3.4 parts). Distillation under reduced pressure gives 110 parts of the product (B.P. 160°—165° C. at 1.5 mm. absolute pressure). It has an  $n_{D}^{25}$  value of 1.4510 and contains 5.07 to 5.17% nitrogen (theoretical for  $C_{11}H_{15}ON$ —5.28%). The product is identified as 7-methyl-7-cyano-9-pentadecanone.

The procedure of this example is used to convert 9-methylheptadec-9-en-11-one to 2-methyl-2-octyl-4-oxodecanonitrile and 10-methylhexacos-10-en-12-one to 2-methyl-2-nonyl-4-oxotridecanonitrile.

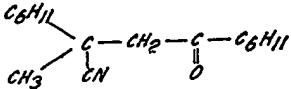
### EXAMPLE 3

A mixture of 1,3-dicyclohexylbut-2-en-1-one (468 parts), 1-methyl-2-pyrrolidinone (400 parts) and sodium cyanide (5 parts) is heated to 200° C. and hydrocyanic acid (57 parts) is added dropwise while the temperature is maintained above 180° C. during the course of the addition. After heating an additional hour after the addition of hydrocyanic acid, the mixture is cooled and treated with aqueous 85% phosphoric acid (8 parts). Distillation under reduced pressure gives a viscous oil (B.P., 230°—275° C. at 3 mm. absolute pressure), which contains 5.4% nitrogen and is identified as the desired product 2-methyl-2,4-dicyclohexyl-4-oxobutanonitrile.

In a similar manner, 2-methyl-2,4-dicyclo-  
phenyl-4-oxobutanonitrile is prepared from  
1,3-dicyclopentylbut-2-en-1-one and hydro-  
cyanic acid. Likewise, by reaction with  
hydrocyanic acid, 2,5,7,9-tetramethyl-2-  
(1,3,5 - trimethylhexyl) - 4 - oxodecanonitrile  
is prepared from 2,4,6,7,10,12,14-hepta-  
methylpentadec-7-en-9-one and 2,6,8-tri-  
methyl - 2 - (3,3,5 - trimethylhexyl) - 4 -  
oxononanonitrile is prepared from 2,4,6,11-  
13-hexamethyltetradec-7-en-9-one.

**EXAMPLE 4**

The procedure of Example 1 is repeated, using 1,3-dicyclohexylbut-2-en-1-one (117 parts), dimethylformamide (111 parts), potassium cyanide (1.6 parts) and hydrocyanic acid (14.2 parts). The product is isolated according to the method of Example 3. The product is identified as the desired nitrile compound having the formula 110

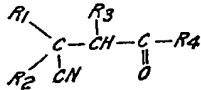


In an analogous way, by reaction with hydrocyanic acid, 2,2,4,4,6-pentamethylnon-6-en-8-one is converted to 2-methyl-2-(2,2,4,4-tetramethylpentyl)-4-oxopentanonitrile. 115

In conclusion, by reason of Section 9 of the Patents Act 1949, reference is directed to U.K. Patent No. 730,209.

WHAT WE CLAIM IS:—

5 1. A compound containing from 13 to 25 carbon atoms and having the formula:



10 in which  $R_1$ ,  $R_2$  and  $R_4$  are alkyl or cyclo-alkyl groups, and  $R_3$  is a hydrogen atom, a methyl group, an ethyl group or a pentyl group.

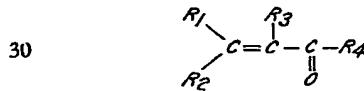
15 2. A compound according to Claim 1, in which  $R_3$  is a hydrogen atom, a methyl group, or an ethyl group, and in which one or two of  $R_1$ ,  $R_2$  and  $R_4$  are methyl groups.

3. The new compound 2,4,8-trimethyl-4-cyano-6-nonenone.

4. The new compound 7-methyl-7-cyano-9-pentadecanone.

20 5. The new compound 2-methyl-2,4-di-cyclohexyl-4-oxobutanonitrile.

25 6. A method for the preparation of a compound as claimed in Claim 1 which comprises bringing together, at a temperature in the range from about  $125^\circ$  to  $275^\circ$  C. and in the presence of an alkaline catalyst capable of generating cyanide ions, hydrocyanic acid and a  $C_{12-24}$   $\alpha,\beta$ -unsaturated ketone of the formula:



30 in which  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are as defined

in Claim 1, the hydrocyanic acid being gradually brought into contact with the ketone at a rate which is substantially that at which it reacts with the ketone.

35

7. A method according to Claim 6, carried out by bringing together, at the reaction temperature, preformed mixtures of (a) the alkaline catalyst and the  $\alpha,\beta$ -unsaturated ketone reactant or the desired cyanoketone product and (b) hydrocyanic acid and the unsaturated  $\alpha,\beta$ -unsaturated ketone reactant.

40

8. A method according to Claim 7, wherein in the catalyst mixture (a) is initially charged to a reaction vessel and the hydrocyanic mixture (b) is then gradually added thereto.

45

9. A method according to any one of Claims 6—8 carried out at a reaction temperature in the range from  $150$  to  $225$ ° C.

50

10. A method according to any one of Claims 6—9, wherein the reaction is carried out in the presence of a volatile inert highly polar organic solvent.

55

11. A method according to any one of Claims 6—10 as applied to the preparation of a compound as claimed in any one of Claims 2—5.

60

12. A method according to Claim 6, when carried out substantially as described in any of the foregoing examples.

13. A  $\beta,\beta$ -disubstituted- $\beta$ -cyanoketone whenever prepared by a method according to any one of Claims 6—12.

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